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NITROGEN IN INDUSTRY*

by

J. B. Farrell**

Production of nitrogen-containing chemicals forms an important segment of the chemical industry. Most of these chemicals are used for fertilizers but a significant proportion have different end-uses, for example, as intermediates in chemical processing sequences. This paper examines the extent of water pollution from these two branches of the nitrogen industry. Also, means for removing nitrogen compounds which enter wastewater are reviewed.

Fixed Nitrogen

The fixation of nitrogen and the manner in which it cycles in the biosphere are reviewed by Delwiche (1970). Nitrogen is fixed by some bacteria and algae, by natural processes in the atmosphere (e.g., lightning), and by industrial fixation. World production of industrially fixed nitrogen amounts to about 33 million tons per year. This is about half as much as all other fixation processes. Nitrogen fixed by combustion processes appears not to be included in these figures. Nelson (1971) quotes data indicating that about 6 million tons of nitrogen per year are fixed in the United States alone by combustion in power plants, heating units, and internal combustion engines.

Delwiche is concerned that the increase in nitrogen fixed by industrial activity may be greater than nature's ability to return nitrogen to the atmosphere by denitrification. This concern should be taken seriously since both fertilizer production and combustion of fuels is steadily increasing.

Most industrially fixed nitrogen is used in fertilizers; only 25 percent is manufactured for industrial uses. These needs are not expected to grow as fast as the market for fertilizer. Consequently, the strain on the nitrogen

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balance in nature comes not from fixed nitrogen produced for industrial uses but from nitrogen fixed for use in fertilizers and nitrogen fixed by combustion processes.

Water Pollution From Fixed Nitrogen

Pollution of water occurs when nitrogen, generally in the form of nitrate, or ammonium, enters ground water, lakes, and rivers. The nitrogen content of unpolluted surface waters is normally less than one milligram per liter and is virtually depleted during the growing season by growing plants and algae (AWWA, 1970). Pollution of water does not ordinarily occur from the primary input streams of fixed nitrogen into the nitrogen cycle. Except for industrial fixation processes, all of the ways in which nitrogen is fixed diffuse the nitrogen over wide areas.

Water pollution by nitrogen compounds generally occurs in the internal recycle between the input and output steps of the nitrogen cycle. The most important contribution to nitrogen pollution of surface waters is the bodily wastes from people. These are conducted rapidly to sewage treatment plants, which do not reduce the nitrogen content, and then directly to the waterways. Municipal wastewaters average about 20 milligrams per liter of nitrogen, chiefly as ammonium. The nutrient load to the surface water is high, and the oxygen demand is also high since ammonium consumes oxygen as it is gradually converted to nitrate. The average daily contribution of nitrogen per capita is about 12 grams. The 200 million people in the United States thus "process" about 1.0 million tons per year of nitrogen, most of which ends up in the nearest available lakes and rivers.

An impressively large internal recycle stream in the nitrogen cycle is the wastes from our farm animal population. As Table 1 shows, the combined pollutional load from this source is approximately ten times the human load, or, for the United States, 10 million tons of nitrogen per year. This nitrogen is deposited on the land where its pollutional impact is not so great. However, the trend to feedlots is changing a diffuse loading into a concentrated loading. The nitrogen loading to surface and groundwater from poorly regulated feedlots can be extremely serious.

TABLE 1

POLLUTIONAL LOAD OF

FARM ANIMALS *

Animal	Numbers per 100 Men	Population Equivalent per Animal	Pollutional Load Relative to Man
Man	100	1.0	100
Horse	1.5	11.3	17
Cow	50	16.4	820
Sheep	13	2.45	32
Hog	26	1.90	50
Hen	190	0.14	27

Source: "Wastes in Relation to Agriculture", unpublished manuscript, U. S. Department of Agriculture", April 1967. Table was constructed from data cited in "Cost of Clean Water, Vol. II".

Approximately 11 million tons of ammonia (as N) are produced annually in the United States (C & EN,1970)and over 75 percent of it is converted to fertilizer products or is applied directly to the soil. While most of this nitrogen does not reach ground or surface water, over-fertilization or application at the wrong time of the year can cause serious nitrogen pollution (Stewart, 1970).

The industrial nitrogen-fixation processes cause relatively minor nitrogen pollution (see below). The remaining industrial processes consume in the United States, no more than about 2.5 million tons of nitrogen. Few of these nitrogen chemicals are used in a fashion that would discharge most of their fixed nitrogen into wastewater. The use of NTA (nitrilotriacetic acid) in detergents was one such use, but this practice has been discontinued. Another such use is acid pickling. Fortunately, nitric acid is not used in large quantities for pickling. There are no concrete data on which to base an estimate, but an educated guess can be made that no more than 10 percent of the nitrogen used by industry or, very approximately, 0.25 million tons, finds its way into wastewater. The rest appears either in gaseous wastes or in products which are discarded on land when their useful life is over. The tonnage lost to wastewater is not insignificant, but it is small compared to all other sources. However, the discharges from chemical plants with a large waste load of nitrogen chemicals will very frequently have a serious impact on local receiving waters.

The Large-Tonnage Chemicals

The nitrogen industry is characterized by the production of a few large-tonnage chemicals which are largely consumed by the fertilizer industry. These chemicals are ammonia, urea, nitric acid, ammonium nitrate, ammonium sulfate, and diammonium phosphate. As noted earlier, fertilizer use of nitrogen accounts for over 75 percent of the ammonia produced.

Despite the large tonnages involved, the pollutional impact of the manufacturing phase of these fertilizer chemicals is relatively light. Barter (1970) has given information on the losses anticipated in the manufacture of

three of these chemicals. The following table has been constructed using his data.

Chemical Produced	Losses of Fixed N to Surroundings lb. N/ton NH_3	% Lost
NH_3	0.5	0.03
urea	3.5-5.0	0.2-0.3
HNO_3	21	1.3

The losses in the manufacture of ammonia are remarkably low. To understand the reason for the low losses, the manufacturing process (Figure 1) must be examined. In current technology, a synthesis gas of hydrogen and nitrogen in a molar ratio of 3 to 1 is produced by steam reforming of methane followed by removal of CO_2. It is important to reduce impurities in the synthesis gas to a minimum. The gas is partially converted to ammonia which is removed by cooling, and the unconverted synthesis gas is recycled and combined with fresh synthesis gas. A small stream of the recycled gas, called a bleed stream or purge gas, must be wasted to prevent gradual buildup of inert gases such as argon. The only place where ammonia is lost is from this bleed stream. Despite the fact that this stream is small, losses are considerable - about 9 pounds of ammonia per ton of ammonia produced. This ammonia is not discharged to the environment because the purge gas is combined with the methane and burned to provide heat for the steam reforming step. The ammonia is oxidized to nitrogen and water. In older plants, the purge gas was washed with water and ammonia was recovered from the wash water. The high solubility of ammonia in water makes removal of ammonia from the gas stream efficient, but ammonia was lost in the bottoms stream, when this dilute ammonia solution was concentrated by distillation.

The losses of fixed nitrogen in the ammonia process are seen to be low chiefly because the volume of purge gas is relatively small. It is then not excessively costly to destroy the residual ammonia in this stream. Even when recovery is practiced, losses are not excessive.

The manufacture of urea has many similarities to ammonia manufacture. Ammonia in substantial excess is mixed with carbon dioxide and reacted to form urea (NH_2CONH_2). There is a substantial recycle stream and a buildup of inerts. Most of the losses come from ammonia lost in a bleed gas stream. The bleed stream is not normally fed to a combustion process. The ammonia losses are approximately the same as is experienced in ammonia manufacture when the ammonia in the purge gas is recovered rather than destroyed. In urea manufacture, the ammonia lost is gaseous, so it does not enter wastewater streams.

A simplified flowsheet for nitric acid manufacture is shown in Figure 2. Ammonia is catalytically oxidized with air, forming nitric oxide (NO) and water. The reaction is highly exothermic. Heat is removed by a heat recovery boiler and by water-cooled heat exchangers. Nitric oxide reacts with oxygen as the gas cools, forming nitrogen dioxide (NO_2). Water condenses in the heat exchanger and absorbs some of the nitrogen dioxide forming nitric acid. The conversion of NO to NO_2 and absorption to form nitric acid is completed in the absorption tower. Residual oxides of nitrogen leave the top of the tower.

Losses from the process are seen from the table above to be substantial. There are two reasons for this: The stream of gas leaving the process is quite large chiefly because of the large amount of nitrogen which enters in the combustion air stream, and the concentration of nitrogen oxides in these gases is large (ca. 1000 ppm). The size of absorber needed to reduce the nitrogen oxides concentration to lower levels would be unreasonably large.

Nitrogen oxides lost in this process do not become a water pollution problem but they are a serious air pollution problem. Newman (1971) observes that nitrogen oxides pollution from nitric acid plants is only 1.0 percent of the total of such discharges. Nevertheless, the high concentration in offgases can cause serious local air pollution.

The production of ammonium nitrate, ammonium sulfate, and diammonium phosphate are simple reactions which produce no substantial waste streams. Pollution is associated with the latter two chemicals when they are produced from by-product ammonia from the coking of coal. The problem arises not in the nature of the reaction but in the ammonia recovery step which precedes the reaction. The by-product gases are laden with impurities so the

ammonia must be scrubbed out by water and regenerated again for reaction with sulfuric or phosphoric acid. The ammonia losses occur in the regeneration step and ammonia is lost in the bottom stream of an ammonia still. Based on data in Industrial Profile No. 1 of the FWQA series "The Cost of Clean Water", approximately 1.0 percent of the ammonia is lost in the wastewater.

The Small-Tonnage Chemicals

The 25 percent of ammonia not used in fertilizers finds its use in the chemical industry. Ammonia itself, and chemicals made from it such as nitric acid and hydrogen cyanide, are used to make intermediate chemicals which are often used to produce others which are still intermediate before a final product results. The chemical forms can become very complicated. When these products enter wastewater, the wastewater renovation problem often becomes complex.

An example of the wastes produced in the manufacture of a moderate tonnage chemical is the relatively simple process for manufacturing urea-formaldehyde molding resins. Urea and formaldehyde enter into a "condensation" reaction, in which a partially crosslinked polymer and water are produced. The materials consumed and the wastes produced are shown in Table 2. The reaction is usually carried out intermittently in large batch reactions.

The waste is ordinarily discharged to a wastewater collection system. Recovery in this and in many similar cases is not simple since the chemicals are partially reacted or would react in a purification step. Loss of nitrogen-containing chemical to the wastewater is large, 4.7 percent of the amount charged. Fortunately, urea is very easily degraded to ammonia in wastewater treatment by the action of the enzyme, urease. Acceptability by municipal wastewater treatment plant operators is high.

An interesting comparison can be made between the fixed nitrogen losses of the by-product ammonia recovery industry and the losses from the manufacture of urea-formaldehyde and melamine-formaldehyde resins (melamine contains about 66% N). About 0.2 billion pounds of fixed nitrogen is used in the manufacture of these resins per year. Approximately 0.8 billion pounds

TABLE 2

Wastes Produced in Manufacture

of Urea-Formaldehyde Resin

I. Chemicals Charged to Batch Reactor

75 lb urea
188 lb formalin (formaldehyde dissolved in water)

II. Products

100 lb urea-formaldehyde resin

III. Waste

113 lb water (from the formalin)
43 lb water (produced in the reaction)
3.5 lb urea (not consumed)
3.5 lb formaldehyde (not consumed)

of by-product ammonia (as N) are recovered per year. According to data in the "Cost of Clean Water" Series (No. 1 and No. 10) both of these industries discharge about the same amount of nitrogen to wastewaters, despite the four-fold difference in the amount of nitrogen processed. The comparison makes it clear that annual production and quantity of pollutant do not always go hand-in-hand.

There are numerous very small tonnage nitrogen-containing chemicals. These obviously cannot be large volume po ters. However, many small tonnage chemicals have physiological activity and often must be totally removed from wastewaters.

Removal of Nitrogen Chemicals from Wastewater

The removal of nitrogen-containing chemicals depends on their chemical structure. Many of them are biodegradable and are converted to ammonium or nitrate ion by biological processes. Biological processing is then generally advisable and if further nitrogen removal is needed, processes specific for nitrate and ammonium ion can be utilized (see below). Many non-biodegradable compounds can be removed by activated carbon. This is an economic solution in many cases. Where carbon treatment fits into the wastewater processing sequence depends on the total composition of the wastewater. Destruction or alteration by oxidants such as chlorine may be the solution. Chlorination is often practiced for cyanide destruction. For some toxic nitrogen-containing compounds, incineration of the entire waste is the only practical solution.

If the nitrogen-containing compounds can be converted into nitrates or ammonium ions, there are a number of processes which can reduce their concentrations. These processes, which are summarized in a recent FWQA (now EPA) publication (1970), are listed in Table 3.

Ammonium Removal

Biological nitrification converts ammonium ion to nitrate ion. Bacteria which develop in the activated sludge process can achieve this conversion. Nitrosomonas oxidize ammonium to nitrite and Nitrobacter oxidize nitrite to nitrate. Oxygen and CO_2 are required for bacterial growth. Nitri-

TABLE 3

Ammonia and Nitrate Removal Processes

Ammonia

- Biological Nitrification
- Stripping With Air
- Selective Ion Exchange
- Chlorination

Nitrate

- Biological Denitrification
- Ion Exchange
- $FeSO_4$ Reduction

fication by this route is often achieved in municipal wastewater treatment. Downing and Hopwood (1964) have worked out the conditions needed. Nitrification in the activated sludge process is favored by longer treatment time, a high degree of aeration, and plug flow. Barth (FWQA 1970) suggests a "two sludge" system where the first stage is a conventional high-rate activated sludge system and the second stage is a nitrification stage. Each stage has separate sludge clarification and circulation.

Ammonium ion can be removed from wastewater by air stripping, provided pH has been raised so that the ammonium ions have been nearly all converted to aqueous ammonia. Ammonia is a very soluble gas so large quantities of air must be used to effect removal. To achieve 90 percent removal at 25°C, about 3000 liters of air are required per liter of water. The huge air demand requires that pressure drop be as low as possible. Water cooling towers have been successfully used for this purpose. Increasing the temperature reduces the air requirement for a given degree of removal. Calcium carbonate scaling, caused by reaction of carbon dioxide in the air with calcium ion in the water, has caused difficulty at Lake Tahoe (FWQA 1970). Additionally, if the wastewater is not hot and ambient air is used as the stripping gas, freezing will be encountered when air temperature falls below 0° C. Air stripping has an advantage over other methods because cost does not go up in direct proportion to the ammonia content of the wastewater.

Synthetic ion exchange resins have poor selectivity for ammonium ion; however, certain naturally occurring minerals (zeolites) are highly selective for this ion. One of these minerals, clinoptilolite, effectively removes NH_4^+ from wastewater (Battelle, 1969). Regeneration is accomplished by using an NaCl, $CaCl_2$, $Ca(OH)_2$ mixture. Ammonia can be stripped from the regenerant so there is no waste brine. The process shows feasibility under conditions where air stripping of the entire effluent is impractical, for example, in below-freezing weather. Because the ammonia has been concentrated into a small regenerant stream, the quantity of air required to strip off the ammonia is proportionately reduced. Consequently, it is economical to heat the air stream to avoid freezing. The ammonium ion in the regenerant can also be destroyed by chlorine (see below).

Ammonium can be destroyed by oxidation with chlorine as shown approximately by the overall equation:

$$3\ Cl_2 + 2NH_4^+ \longrightarrow N_2 + 6HCl + 2H^+$$

the actual consumption of chlorine is 4 moles of chlorine per two moles of ammonia, or 10 grams of chlorine per gram of ammonia (as N). This is higher than shown by the overall reaction, indicating formation of a higher oxidation state for nitrogen. This oxidation actually forms chloramines as intermediate products:

$$Cl_2 + NH_3^+ \longrightarrow HCl + NH_2Cl \text{ monochloramine}$$

$$Cl_2 + NH_2Cl \longrightarrow HCl + NHCl_2 \text{ dichloramine}$$

$$Cl_2 + NHCl_2 \longrightarrow HCl + NCl_3 \text{ trichloramine}$$

Conditions can be chosen to minimize formation of trichloramine (Bishop, March 1971).

Chlorination to remove ammonium produces hydrochloric acid in solution which causes a pH drop and increases the chloride concentration in the effluent. The process, however, has very low capital requirements. The chlorine can be made by electrolysis of brine to make sodium hypochlorite. When this is done, the acidity added to the water is halved.

Nitrate Removal

Nitrates can be reduced by many bacteria which use the oxygen in the nitrate for their metabolism. Nitrites are produced first but they are usually rapidly reduced to nitrogen gas by further bacterial action. A source of organic food must be present for denitrification.

Denitrification has been demonstrated by Barth and others (FWQA, 1970) in a "three sludge" biological system. A two sludge system produces a nitrified effluent (see above). Denitrification is carried out in a third stage, comprising an anaerobic stirred vessel to which an organic food is added. This third stage has a separate clarifier and sludge return. The preferred organic food is methanol. About 3 grams per gram of nitrate-N is needed.

Denitrification can be carried out in a packed bed of stone, sand, or carbon. St. Amant and McCarty (1969) have demonstrated removal of nitrates from irrigation return flow in a bed made up of one-inch gravel.

Nitrates have been removed from wastewater by ion exchange. Resins which are both selective for nitrate and capable of regeneration have not

been developed. Consequently, the resins take out all of the other anions present as well as nitrate. Regenerant brine requirements are large, and a high nitrate brine requires disposal.

Nitrates can be reduced to nitrogen and some nitrous oxide by ferrous sulfate (Gunderloy et al, 1968). A voluminous sludge of ferrous-ferric hydroxide results. The process may have value in special situations.

Summary

Nitrogen produced by industry represents only a portion of the fixed nitrogen distributed to soil and water. When nitrogen produced for fertilizer is eliminated from consideration, the amount remaining is unlikely to be responsible for a general overabundant loading of soil and water, even assuming large losses. The problem of nitrogen in industry then is one of point sources of pollution.

The largest tonnage processes in which ammonia is produced or used as a reactant are characterized by low fixed-nitrogen losses. Ammonia is lost in wastewater streams rather than in gaseous effluents. Nitrogen oxides are frequently present in the gaseous effluents. Gaseous pollutants, particularly nitrogen oxides, can present serious local air pollution problems, but are not serious water pollution problems, unless large bodies of water are nearby.

Small production or consumption of nitrogen does not mean little pollution. Losses from small facilities can be large in total quantity lost. Recovery can be impractical because of complexity of separation or partial reaction of the nitrogen-bearing compound.

Some nitrogen-containing chemicals are physiologically active. Even when losses are small, they may have great pollutional impact unrelated to their nitrogen content. There is a serious problem, but different and separate from the nitrogen-pollution problem.

Means are available for destroying, removing, or biologically degrading most nitrogen-bearing compounds. Incineration is a last resort. If the nitrogenous compounds can be converted to ammonium or nitrate, means are available for removing them from water or converting them to nitrogen gas.

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No. 1 Blast Furnaces and Steel Mills
No. 2 Motor Vehicles and Parts
No. 3 Paper Mills, except Building
No. 4 Textile Mill Products
No. 5 Petroleum Refining
No. 6 Canned and Frozen Fruits and Vegetables
No. 7 Leather Tanning and Finishing
No. 8 Meat Products
No. 9 Dairies
No.10 Plastic Materials and Resins

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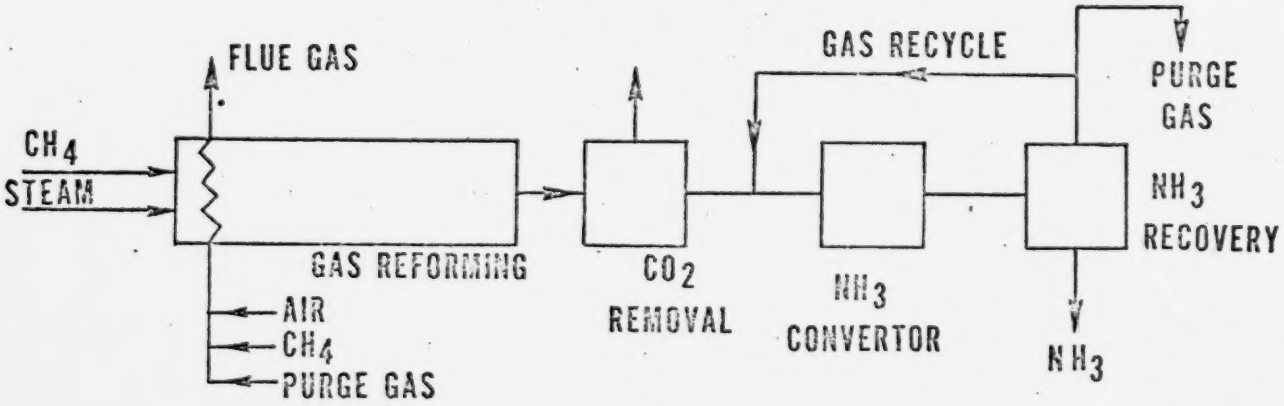
FIGURE 1

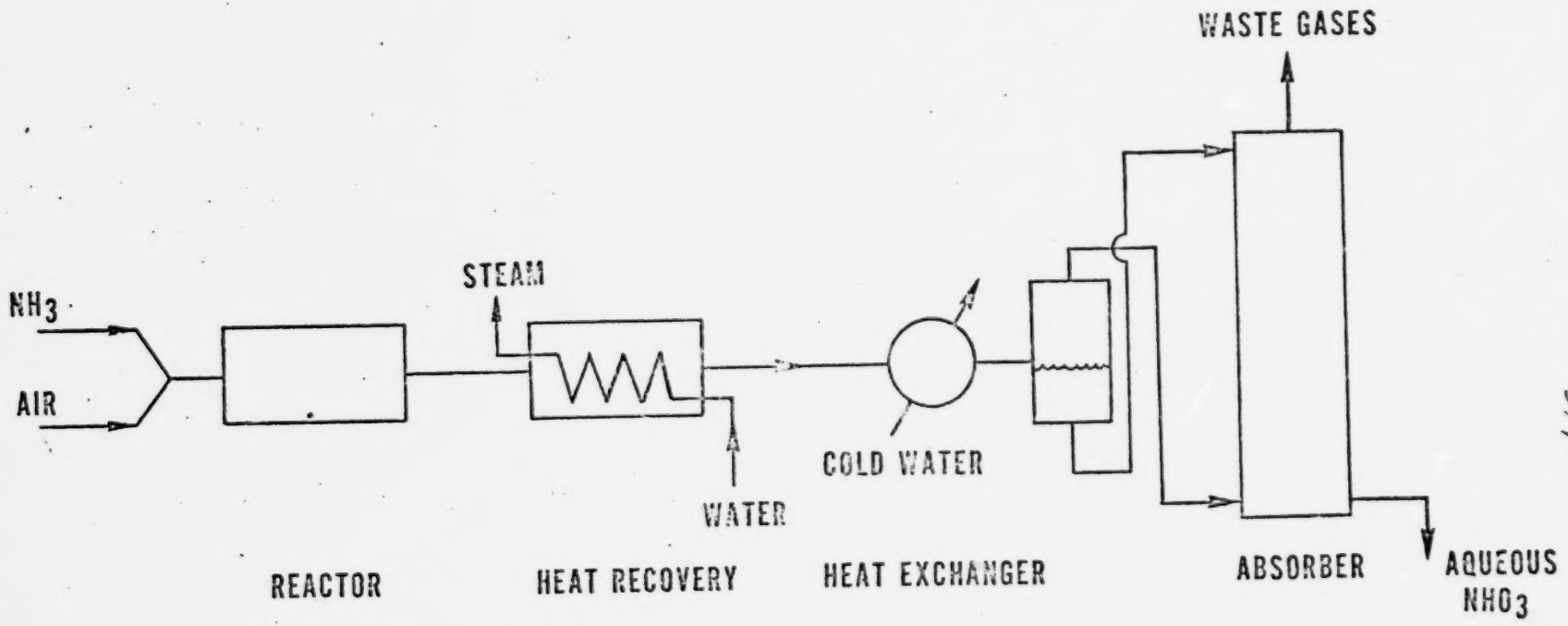
SCHEMATIC REPRESENTATION OF PROCESS FOR AMMONIA SYNTHESIS



CHEMICAL REACTION: $N_2 + 3H_2 \longrightarrow 2NH_3$

FIGURE 2

SCHEMATIC FLOWSHEET FOR NITRIC ACID MANUFACTURE



CHEMICAL REACTION :

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$